Supplementary data

Picolylamine-Ni(II) Complex Attached on 1,3,5-Triazine-Immobilized Silica-Coated Fe_3O_4 Core/Shell Magnetic Nanoparticles as an Environmental Friendliness and Recyclable Catalyst for One-Pot Synthesis of Substituted Pyridine Derivatives

Sobhan Rezayati[a], Fatemeh Kalantari[a], Ali Ramazani*[a,b]

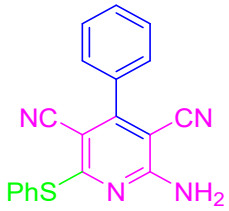
[a]*Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan 45371-38791, Iran*

[b]*Department of Biotechnology, Research Institute of Modern Biological Techniques (RIMBT), University of Zanjan, Zanjan 45371-38791, Iran*

Corresponding author :aliramazani@znu.ac.ir; aliramazani@gmail.com

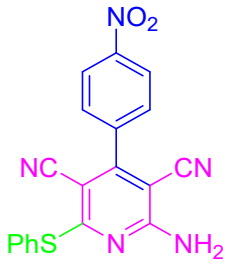
Table S1. The XRD data for the Ni^{II}-Picolylamine/TCT/APTES@SiO_2@Fe_3O_4

Entry	2θ	Peak width (FWHM)	Miller indices			Particle size	Inter-planer distance
			h	k	l		
1	30.45	0.3444	1	0	4	23.9	0.270
2	35.44	0.2460	1	1	0	33.9	0.251
3	35.68	0.2460	1	1	0	33.9	0.251
4	43.24	0.2952	2	0	2	29.0	0.207
5	53.69	0.5904	1	1	6	15.1	0.169
6	57.14	0.2640	1	2	2	33.9	0.160
7	62.86	0.2952	2	1	4	31.6	0.148



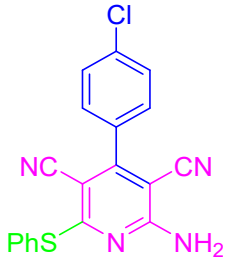
2-Amino-4-phenyl-6-(phenylthio)pyridine-3,5-dicarbonitrile (4a)

Pale yellow solid, FT-IR (KBr): ν 3554, 3478, 3062, 2970, 2217, 1651, 1625, 1441, 1263, 1037, 757 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.22-7.54 (m, 10H, Ar-H), 5.48 (s, 2H, NH_2). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 87.4, 114.7, 115.2, 127.1, 128.4, 129.0, 129.3, 129.9, 130.9, 133.1, 135.7, 158.3, 159.2, 169.0.



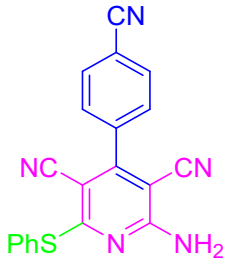
2-Amino-4-(4-nitrophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4b)

Yellow solid, IR (KBr): *v* 3424, 3333, 2213, 1638, 1459, 1317, 1262, 1022, 848, 745 cm^{-1}. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 8.39 (d, 2H, J = 8.25 Hz, Ar-H), 7.83–7.90 (m, 5H, Ar-H), 7.48-7.57 (m, 4H, Ar-H, NH_2). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 87.4, 93.5, 115.0, 115.4, 124.3, 127.3, 129.9, 130.2, 131.7, 135.2, 140.6, 157.1, 159.9, 166.6.



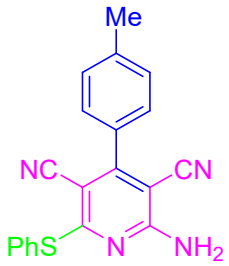
2-Amino-4-(4-chlorophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4c)

Green solid, IR (KBr): *v* 3486, 3415, 2213, 1633, 1494, 1259, 1093, 805, 741 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.25-7.52 (m, 9H, Ar-H), 5.47 (s, 2H, NH_2). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 87.1, 95.7, 114.9, 129.3, 129.4, 129.8, 130.0, 131.4, 135.7, 137.4, 142.1, 157.1, 159.1, 169.3



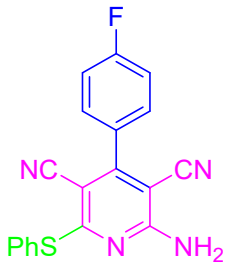
2-Amino-4-(4-cyanophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4d)

Pale yellow solid, IR (KBr): *v* 3415, 3318, 2234, 2217, 1636, 1464, 1263, 1022, 749 cm^{-1}. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 8.05 (d, 2H, J = 7.5, Ar-H), 7.89 (s, 2H, NH_2), 7.76 (d, 2H, J = 7.5, Ar-H), 7.48-7.56 (m, 5H, Ar-H). ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 87.3, 93.4, 113.5, 115.1, 115.4, 118.6, 127.3, 130.0, 133.1, 135.2, 138.9, 157.5, 159.9, 166.6



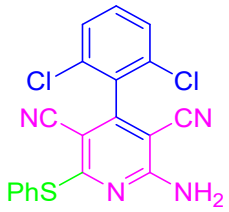
2-Amino-4-(4-methylphenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4e)

Pale yellow solid, IR (KBr): *v* 3474, 3336, 2214, 1625, 1438, 1261, 1023, 809, 755 cm^{-1}. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 2.42 (s, 3H, Me), 5.54 (s, 2H, NH_2), 7.25 (m, 2H, Ar-H), 7.32-7.35 (m, 7H, Ar-H). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ18.3, 21.4, 58.3, 87.3, 114.9, 115.3, 127.2, 128.4, 129.3, 129.7, 130.2, 135.7, 141.4, 158.5, 159.3, 160.9



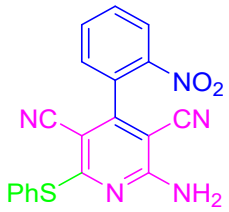
2-Amino-4-(4-fluorophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4f)

Cream solid, IR (KBr): *v* 3493, 3411, 2918, 3223, 2216, 1633, 1441, 1231, 1021, 826, 758 cm^{-1}. ^{1}H-NMR (62.5 MHz, $CDCl_3$): δ 7.30-7.79 (m, 9H, Ar-H), 5.59 (s, 2H, NH_2). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 87.7, 93.9, 115.4, 115.7, 116.1, 119.4, 129.9, 130.1, 130.7, 131.4, 131.6, 158.1, 160.0, 161.9, 166.5.



2-Amino-4-(2,6-dichlorophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4j)

Pale green solid, IR (KBr): *v*3462, 3357, 3075, 2872, 2208, 2176, 1659, 1250, 1023, 722, 688 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.31-7.51 (m, 8H, Ar-H), 5.91 (s, 2H, NH_2). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 87.3, 93.4, 111.7, 114.9, 118.3, 119.1, 120.0, 126.3, 126.6, 131.4, 135.1, 151.2, 159.4, 159.7, 170.0



2-Amino-4-(2-nitrophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (4l)

Pale yellow solid, IR (KBr): *v* 3464, 3407, 3127, 2216, 1623, 1439, 1345, 1256, 1127, 1109, 855, 747 cm^{-1}. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 8.34 (d, 2H, J = 7.75, Ar-H), 7.42-7.99 (m, 10H, Ar-H, NH_2). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ86.3, 93.8, 114.3, 114.8, 121.1, 127.7, 129.1, 129.5, 130.5, 131.1, 136.1, 143.8, 146.1, 149.2, 157.4, 160.5, 161.6.

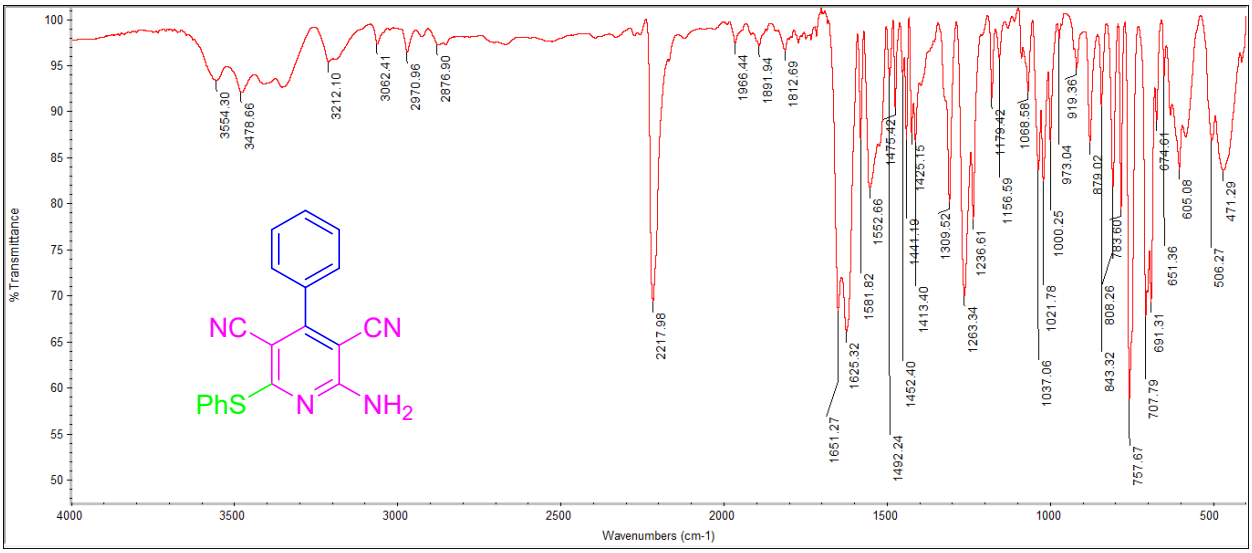


Figure S1. FT-IR spectrum of 2-amino-4-phenyl-6-(phenylthio)pyridine-3,5-dicarbonitrile (**4a**)

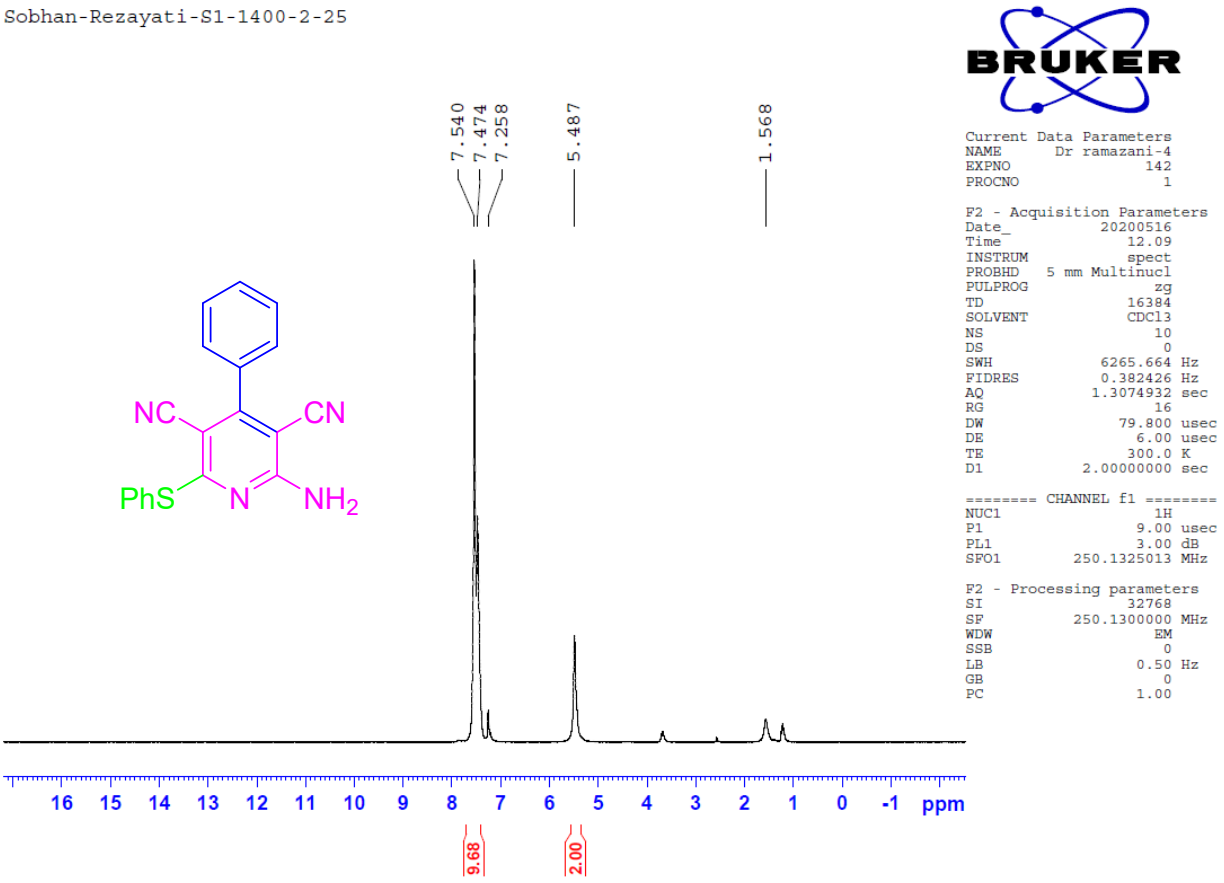


Figure S2. ^{1}H NMR spectrum of 2-amino-4-phenyl-6-(phenylthio)pyridine-3,5-dicarbonitrile (**4a**)

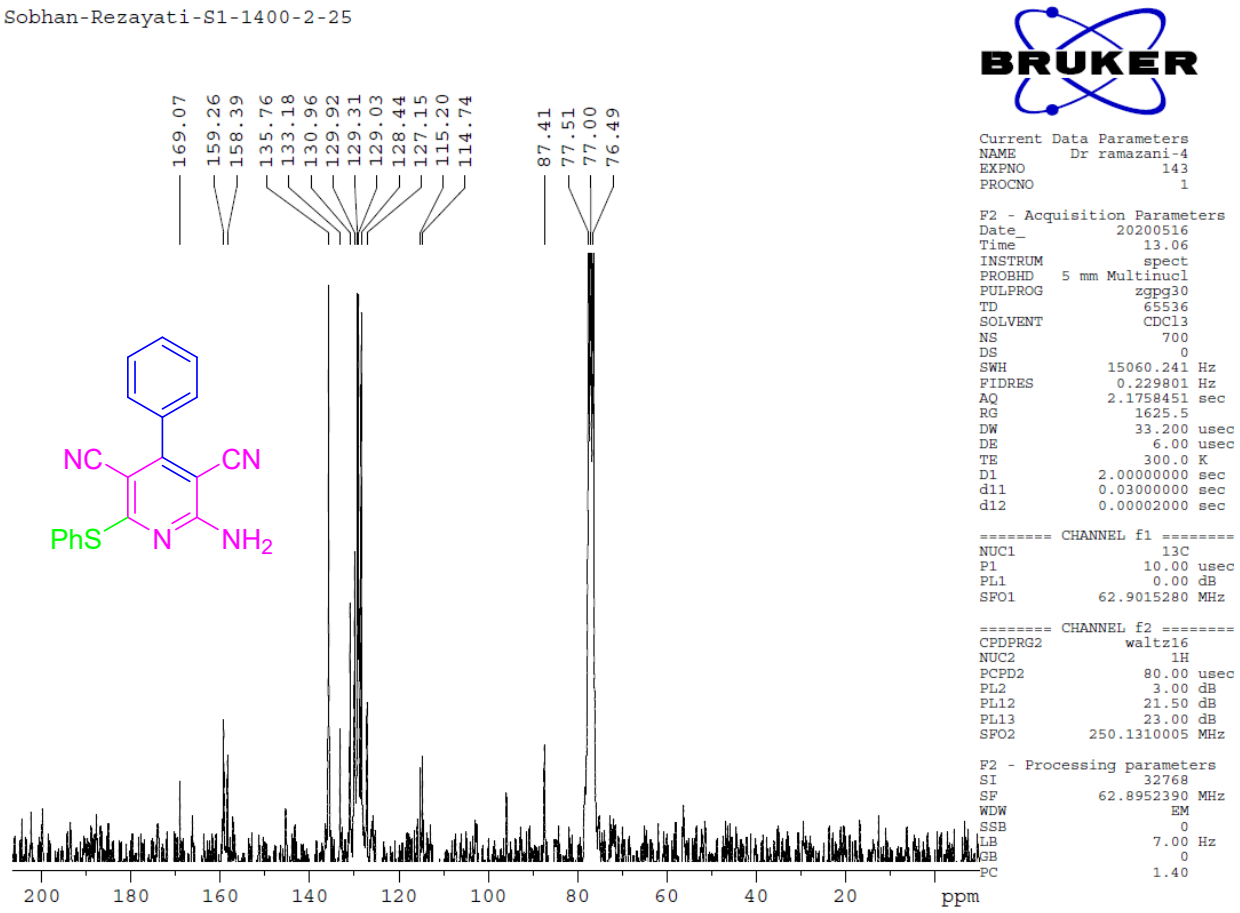


Figure S3. ^{13}C NMR spectrum of 2-amino-4-phenyl-6-(phenylthio)pyridine-3,5-dicarbonitrile (**4a**)

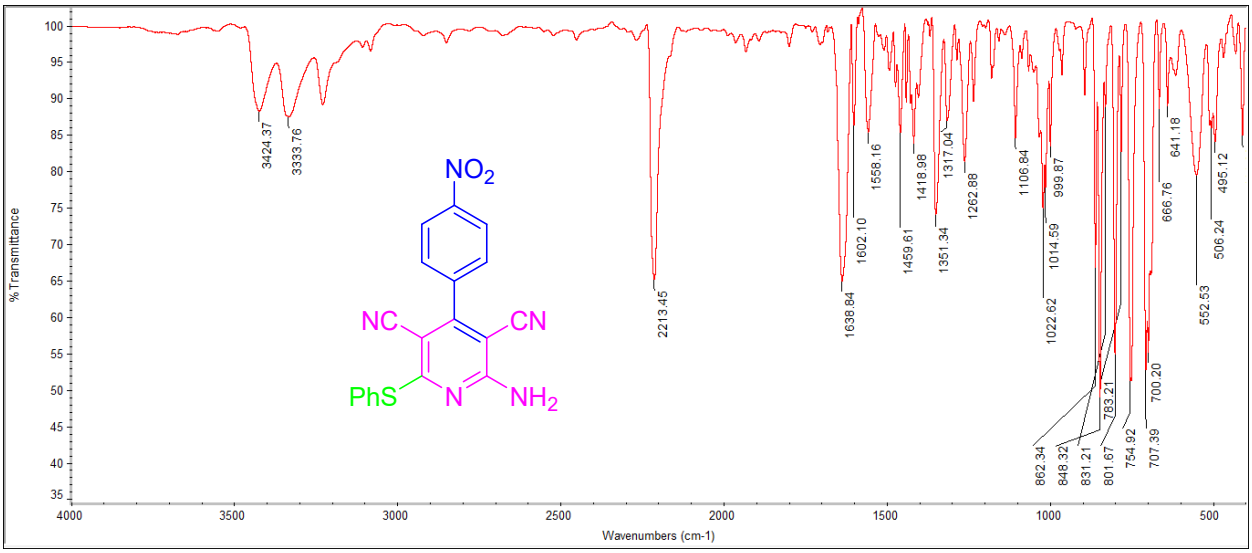


Figure S4. FT-IR spectrum of 2-amino-4-(4-nitrophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (**4b**)

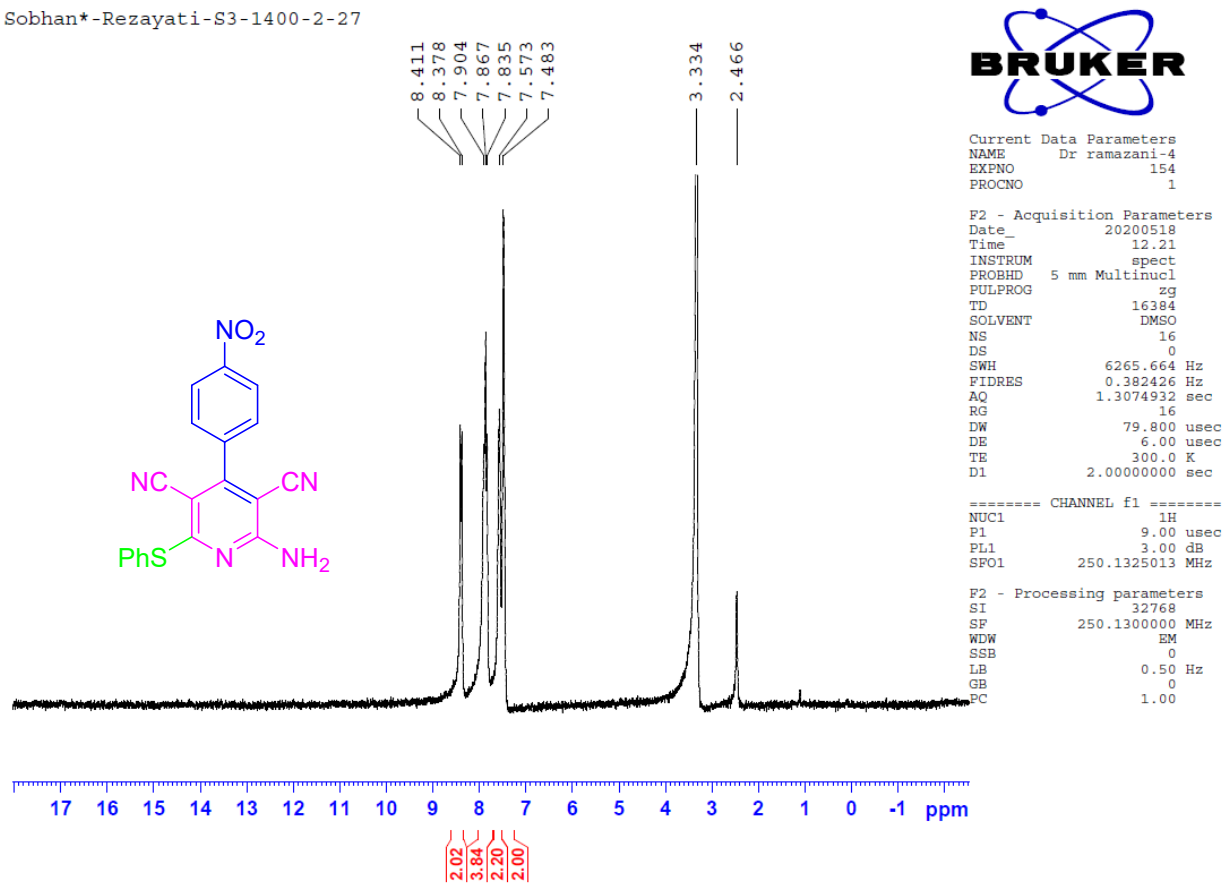


Figure S5. ^{1}H NMR spectrum of 2-amino-4-(4-nitrophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (**4b**)

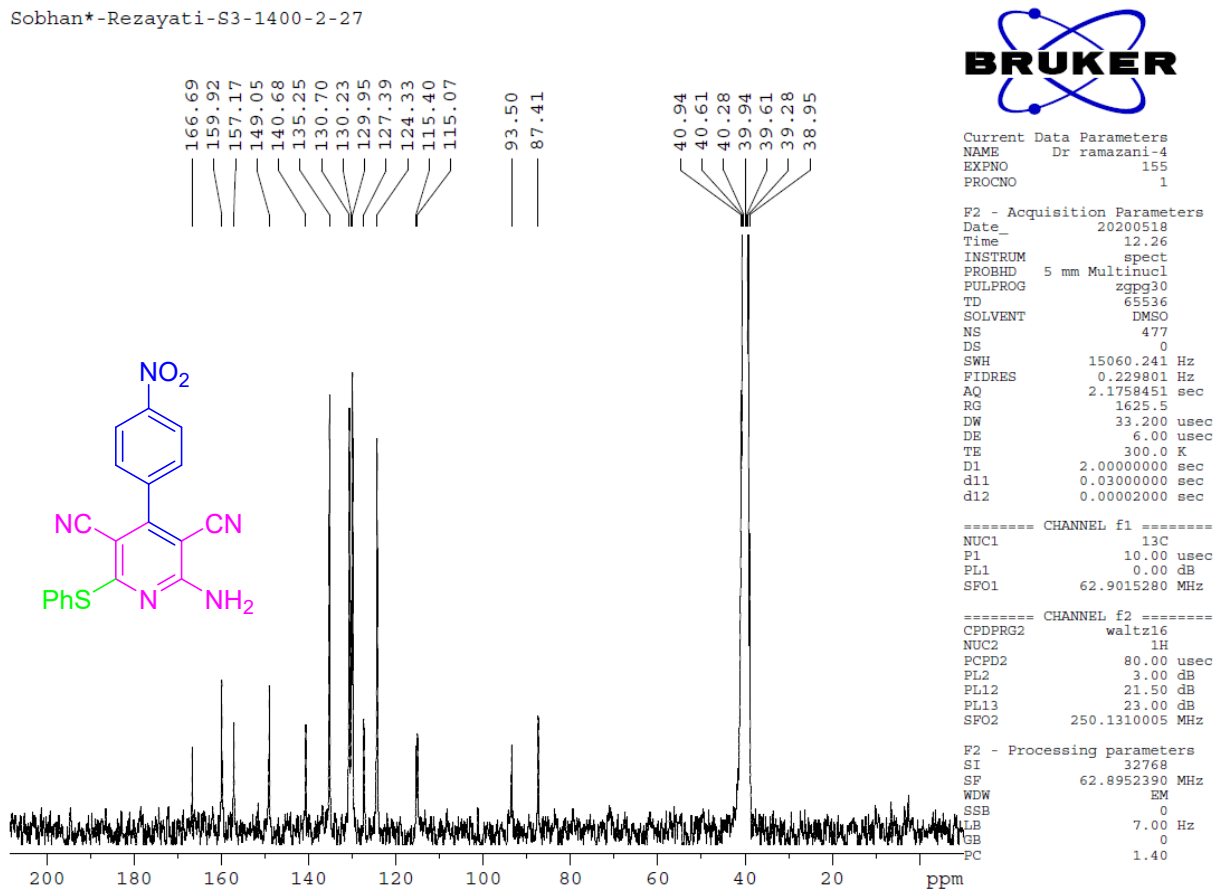


Figure S6. ^{13}C NMR spectrum of 2-amino-4-(4-nitrophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (**4b**)

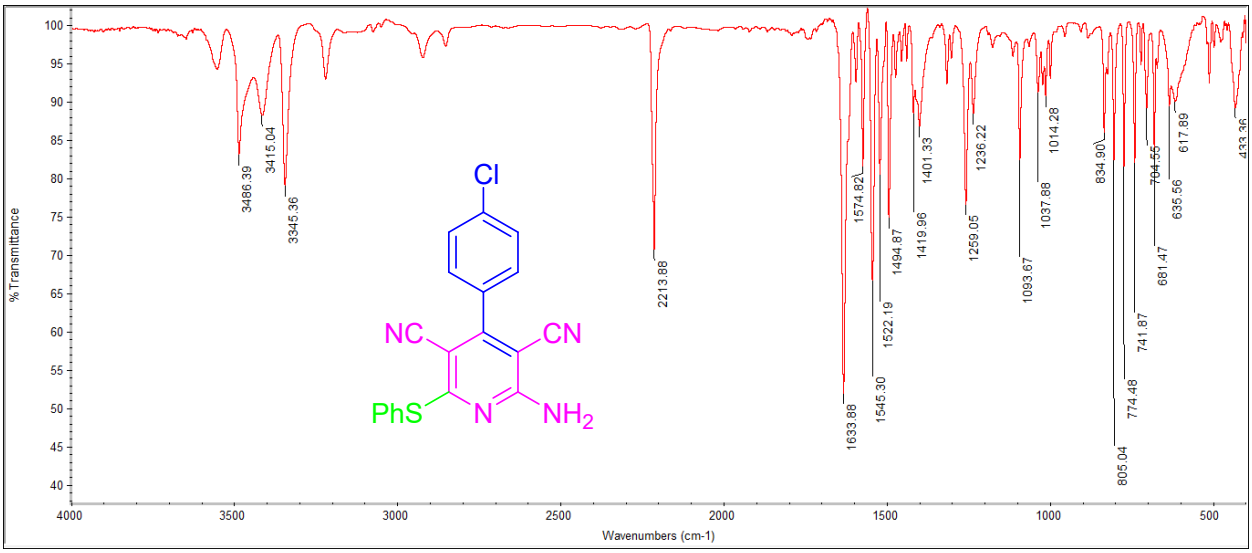


Figure S7. FT-IR spectrum of 2-amino-6-((4-chlorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4c**)

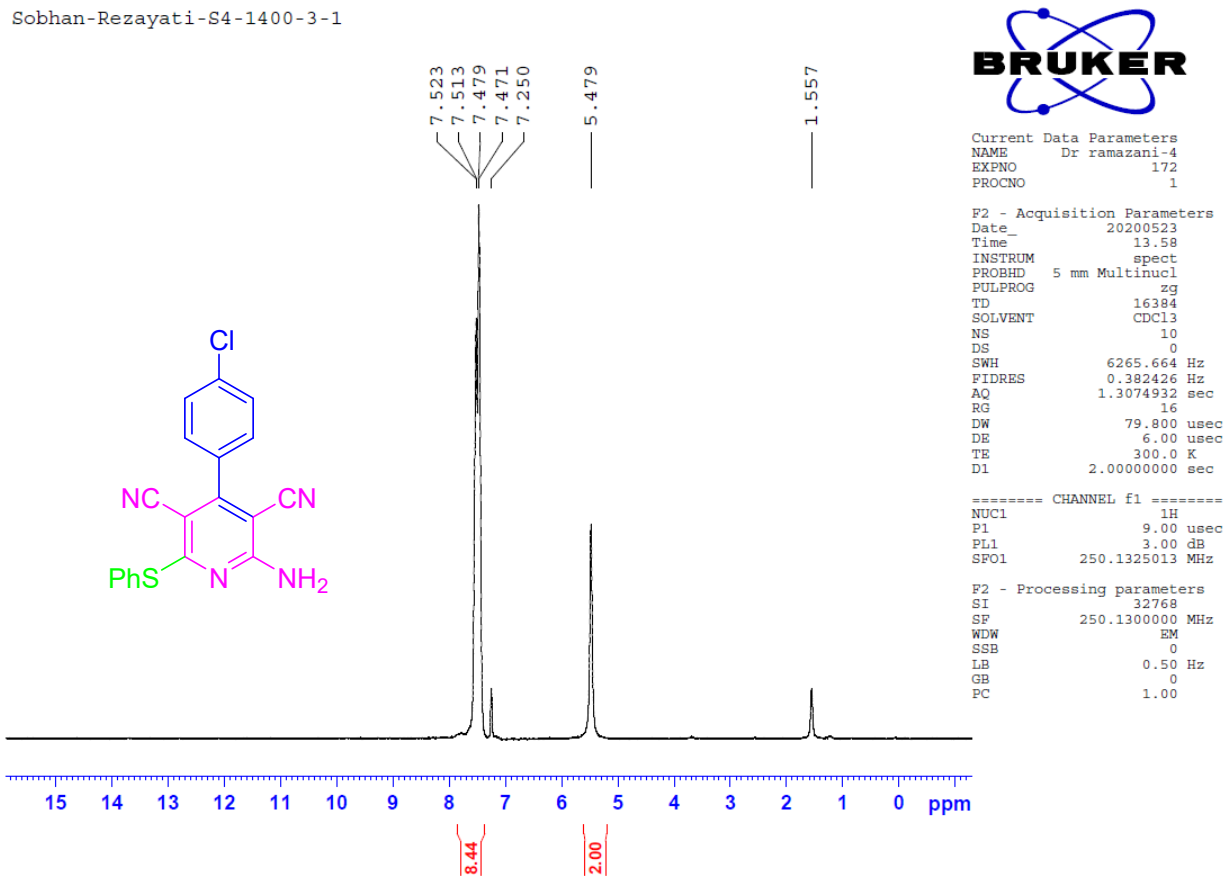


Figure S8. ^{1}H NMR spectrum of 2-amino-6-((4-chlorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4c**)

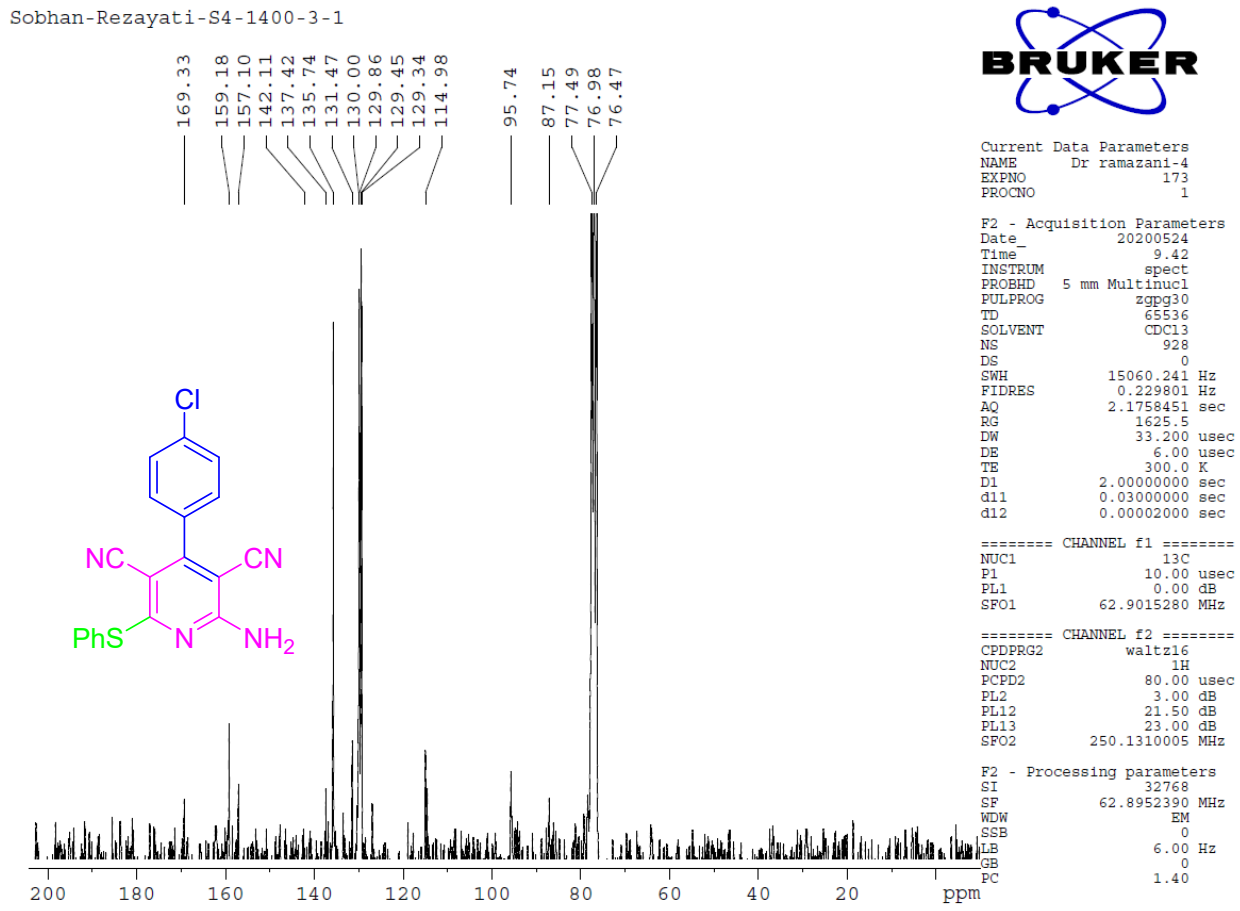


Figure S9. ^{13}C NMR spectrum of 2-amino-6-((4-chlorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4c**)

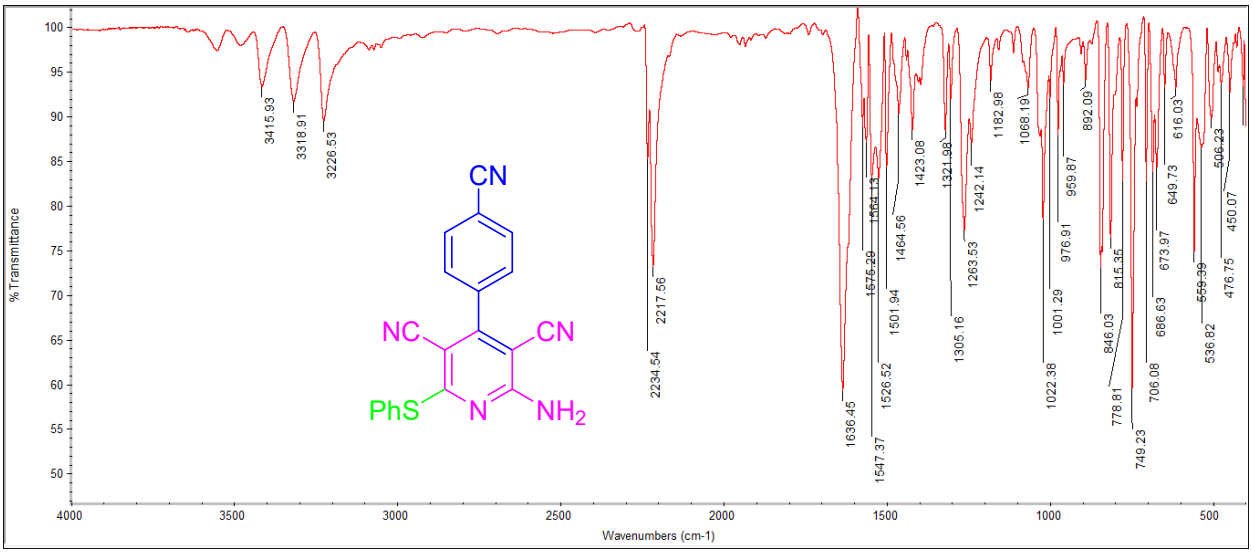


Figure S10. FT-IR spectrum of 2-amino-6-((4-cyanophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4d**)

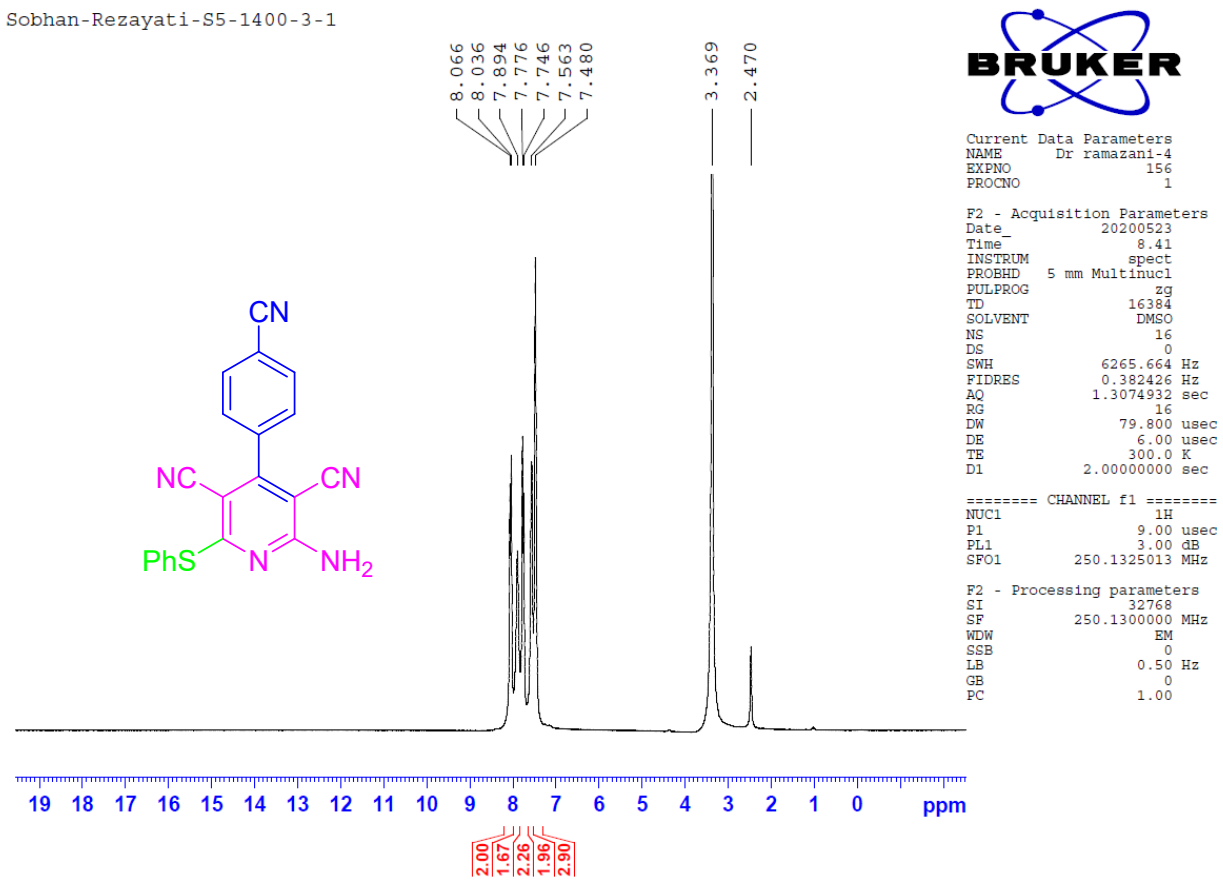


Figure S11. ^{1}H NMR spectrum of 2-amino-6-((4-cyanophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4d**)

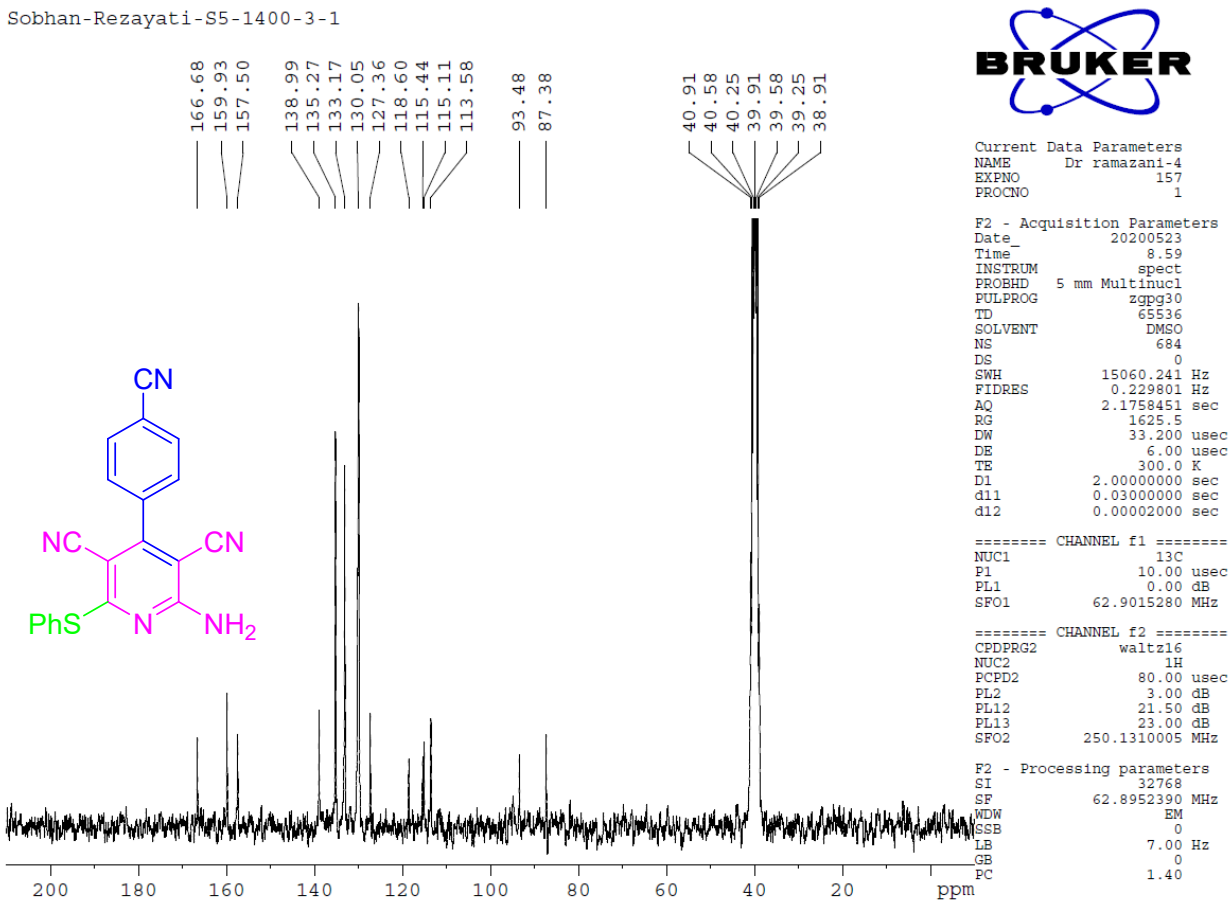


Figure S12. ^{13}C NMR spectrum of 2-amino-6-((4-cyanophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4d**)

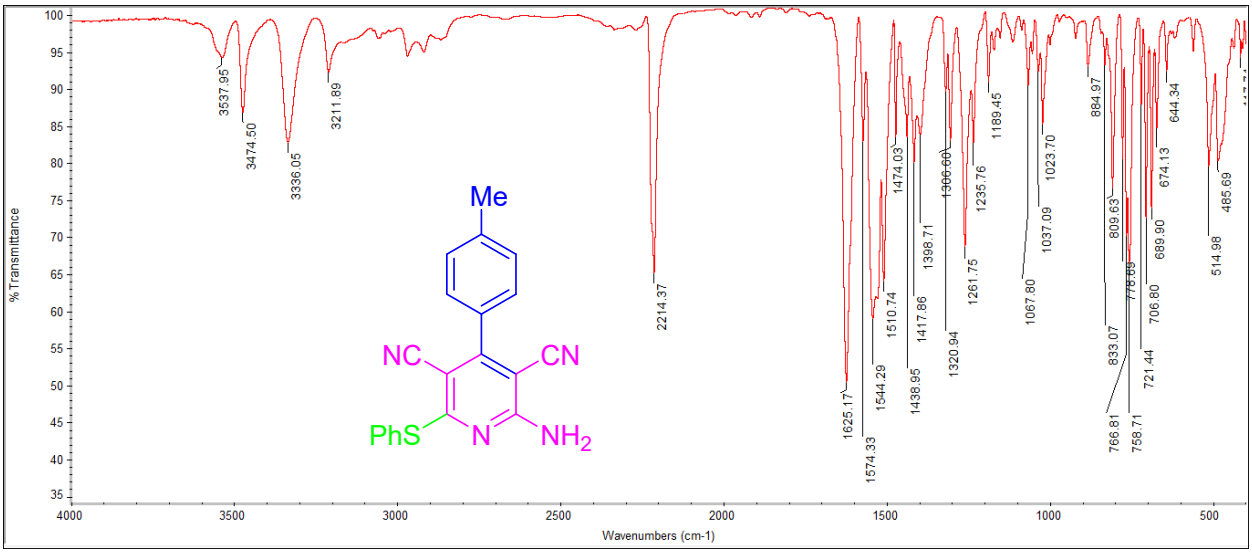


Figure S13. FT-IR spectrum of 2-amino-6-((4-methylphenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4e**)

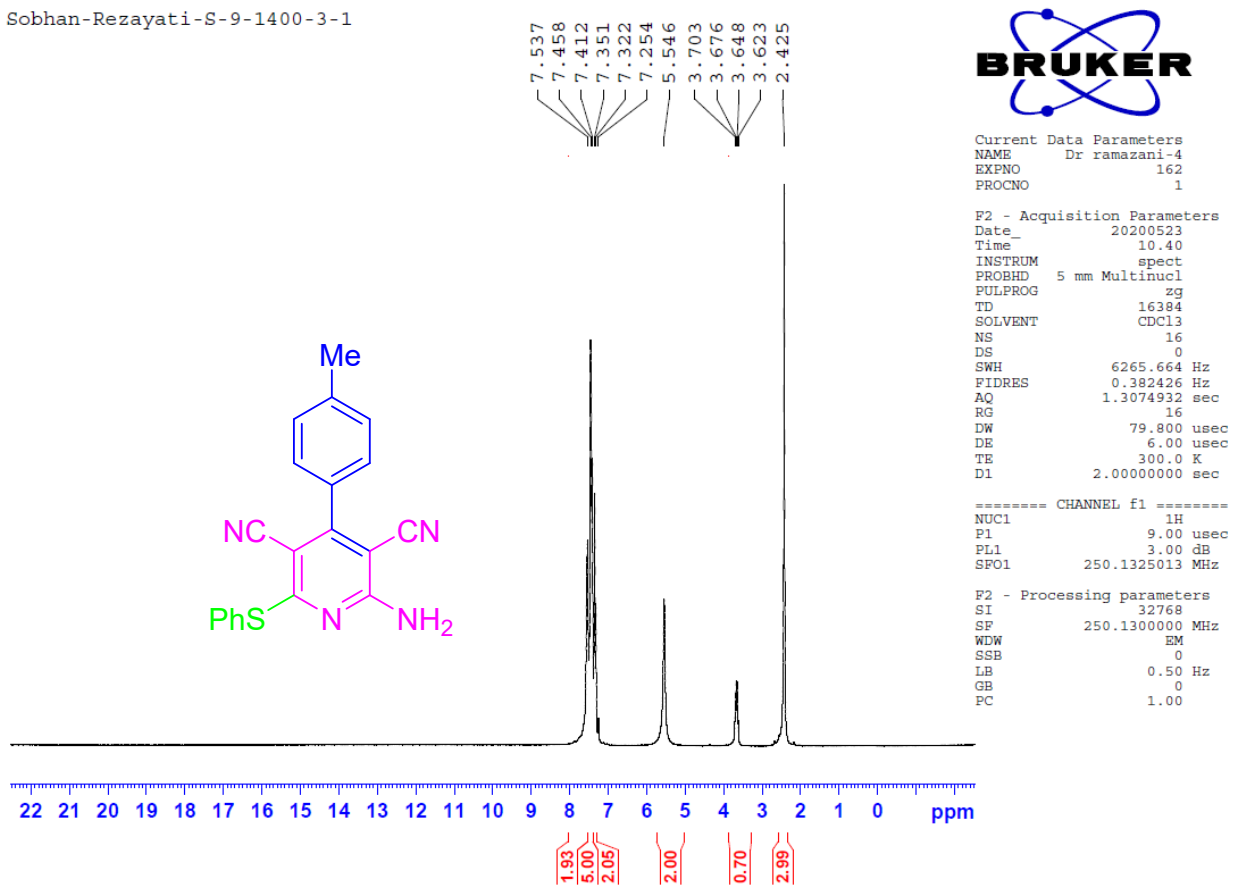


Figure S14. [1]H NMR spectrum of 2-amino-6-((4-methylphenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4e**)

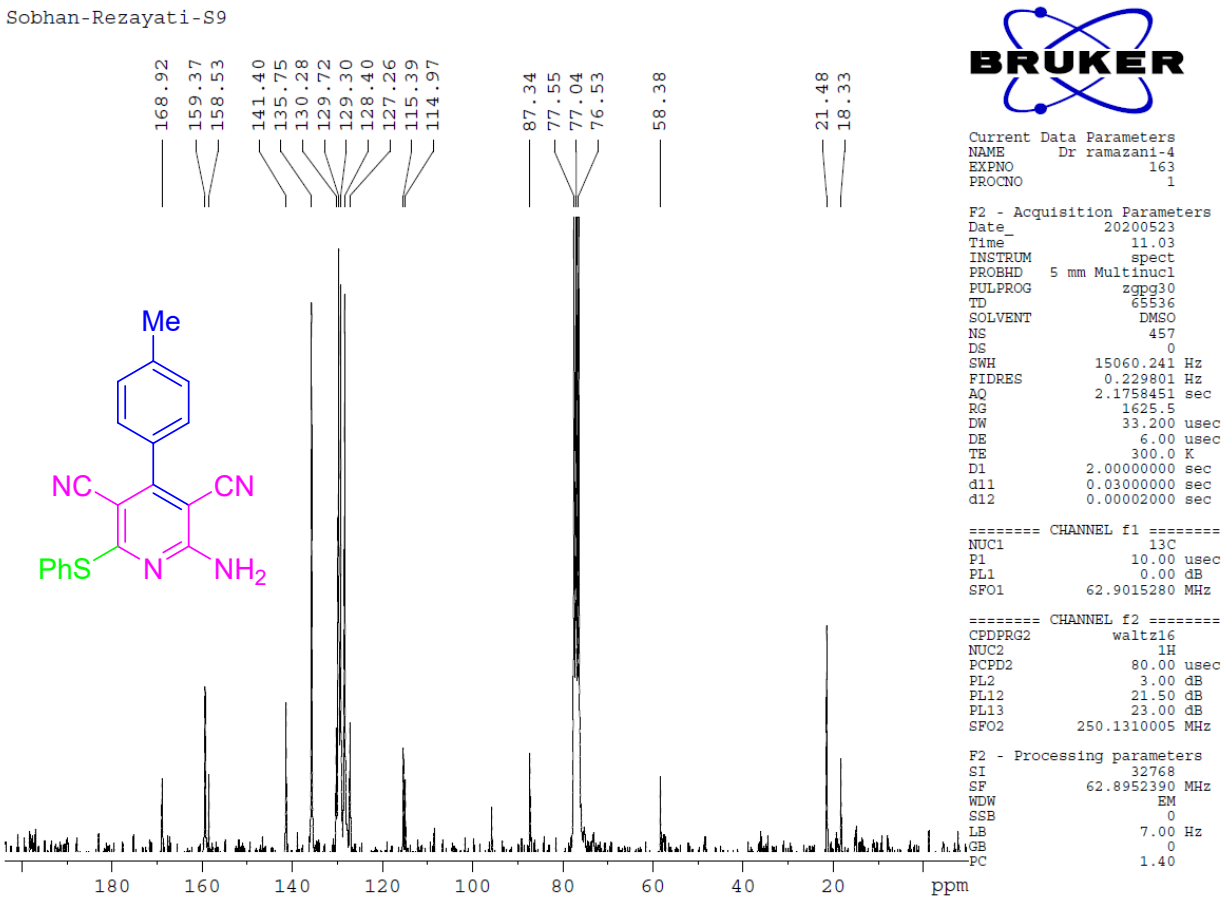


Figure S15. ^{13}C NMR spectrum of 2-amino-6-((4-methylphenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4e**)

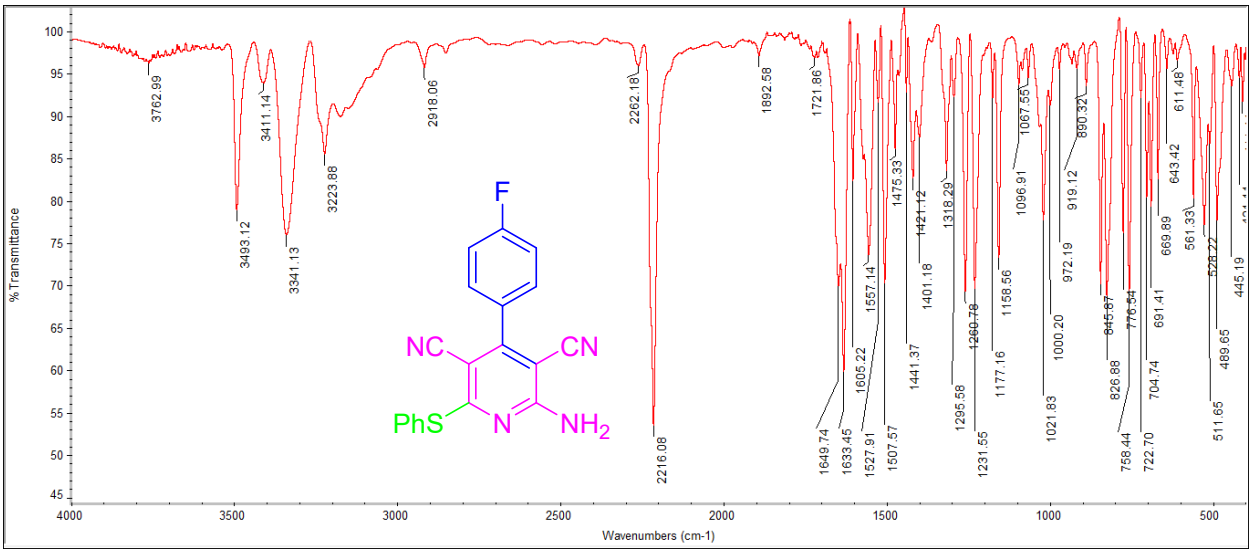


Figure S16. FT-IR spectrum of 2-amino-6-((4-fluorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4f**)

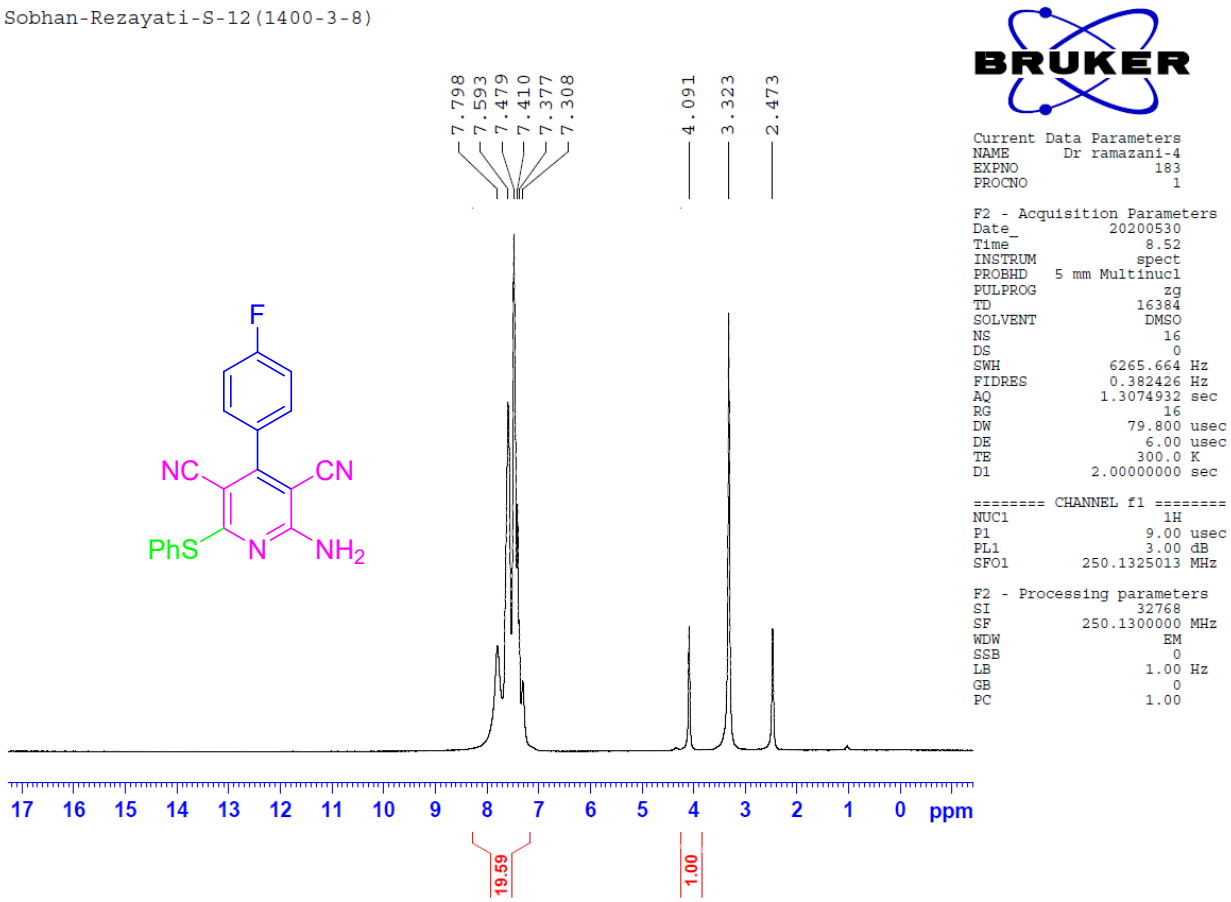


Figure S17. ^{1}H NMR spectrum of 2-amino-6-((4-fluorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4f**)

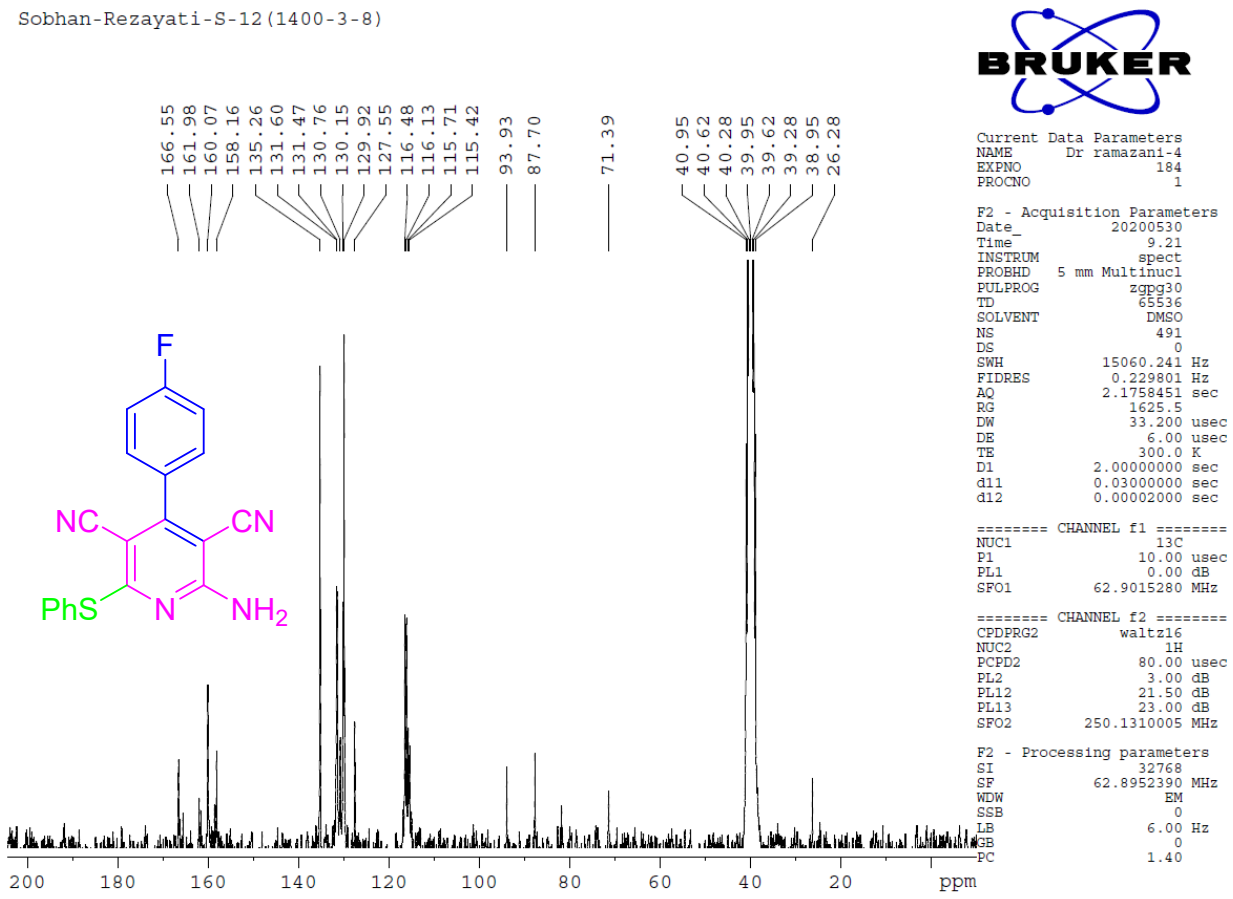


Figure S18. ^{13}C NMR spectrum of 2-amino-6-((4-fluorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4f**)

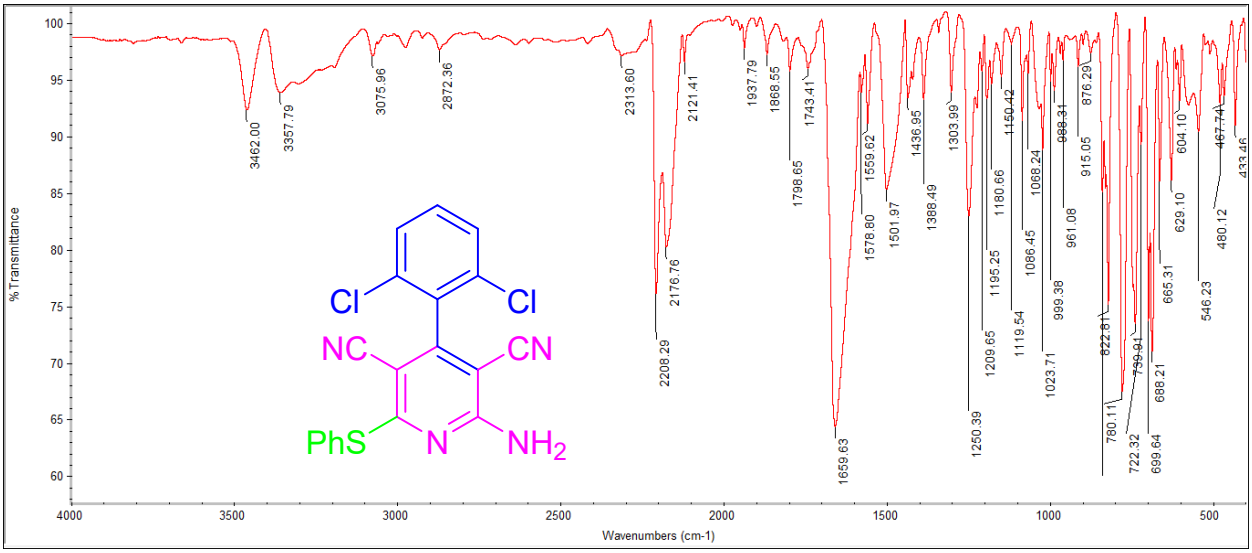


Figure S19. FT-IR spectrum of 2-amino-6-((2,6-dichlorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4j**)

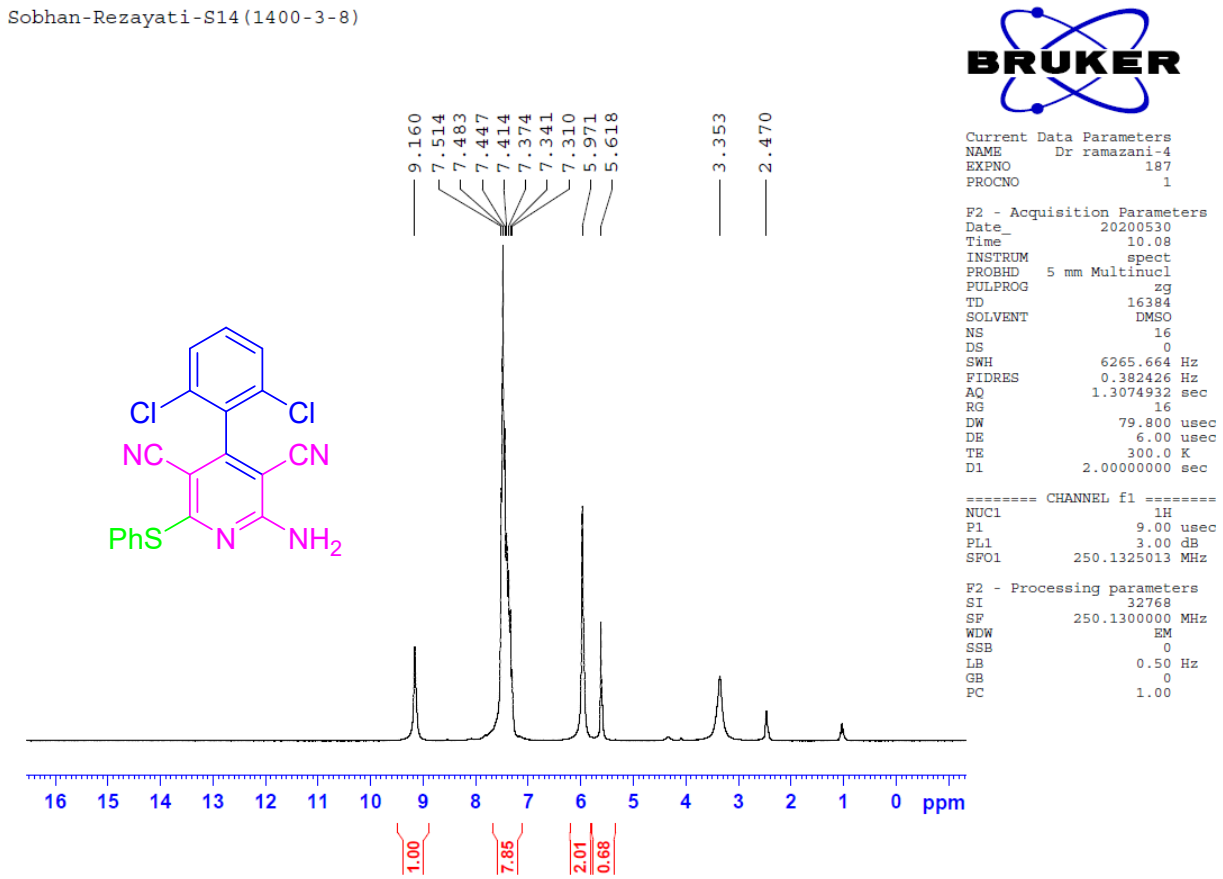


Figure S20. [1]H NMR spectrum of 2-amino-6-((2,6-dichlorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4j**)

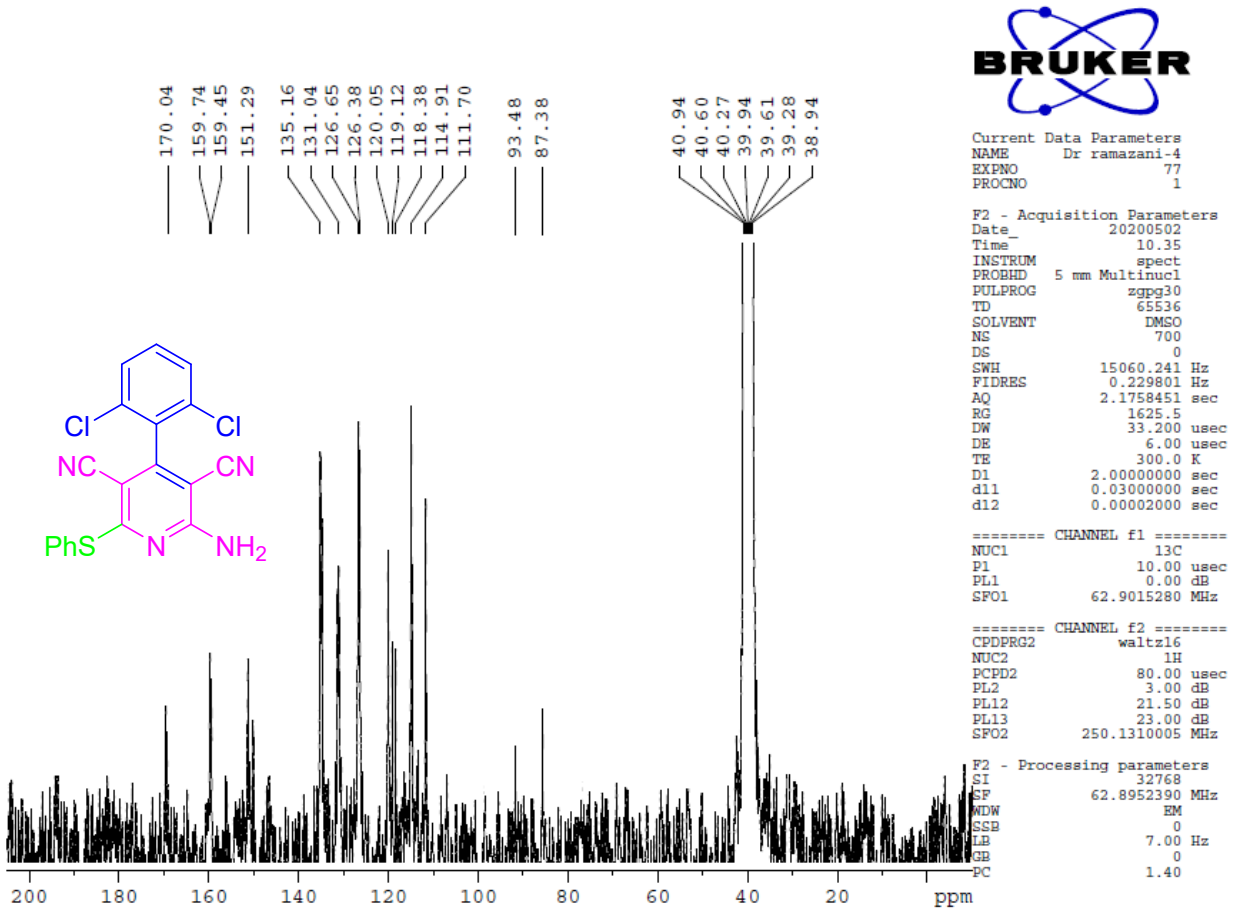


Figure S21. ^{13}C NMR spectrum of 2-amino-6-((2,6-dichlorophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4j**)

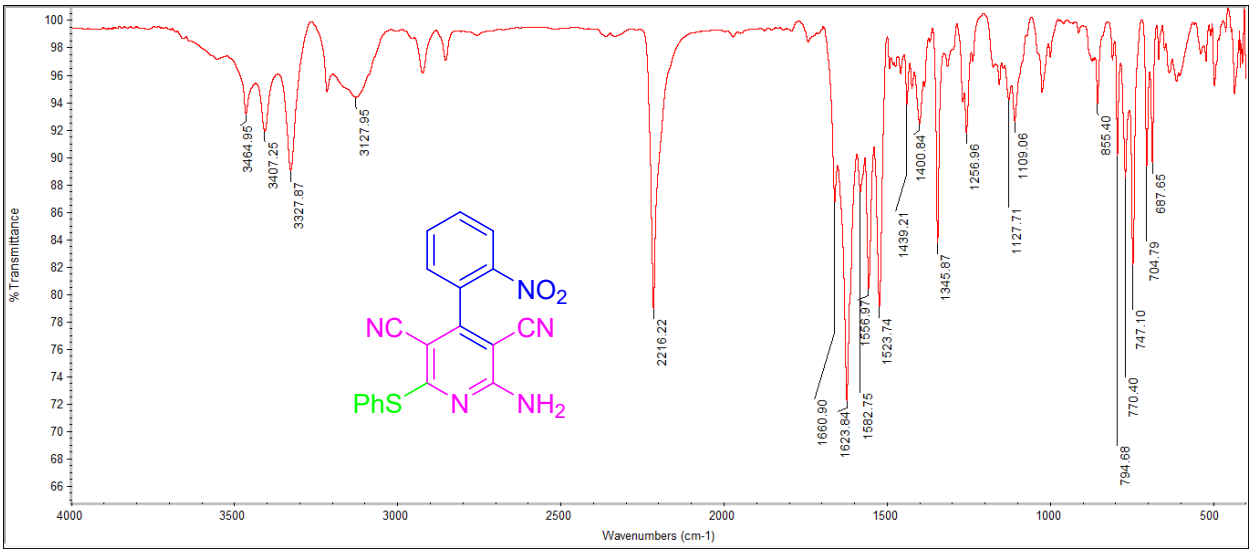


Figure S22. FT-IR spectrum of 2-amino-6-((2-nitrophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4l**)

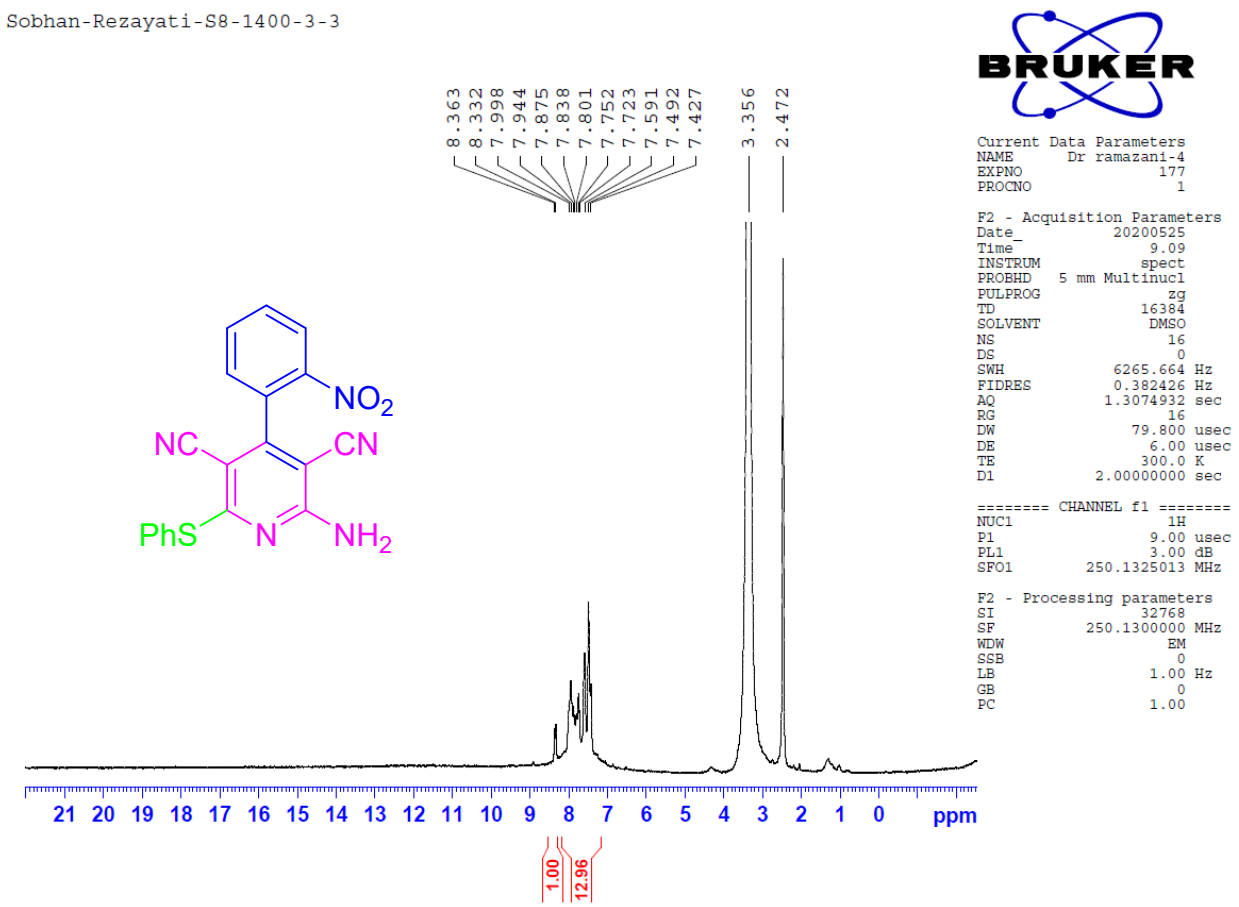


Figure S23. ^{1}H NMR spectrum of 2-amino-6-((2-nitrophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4l**)

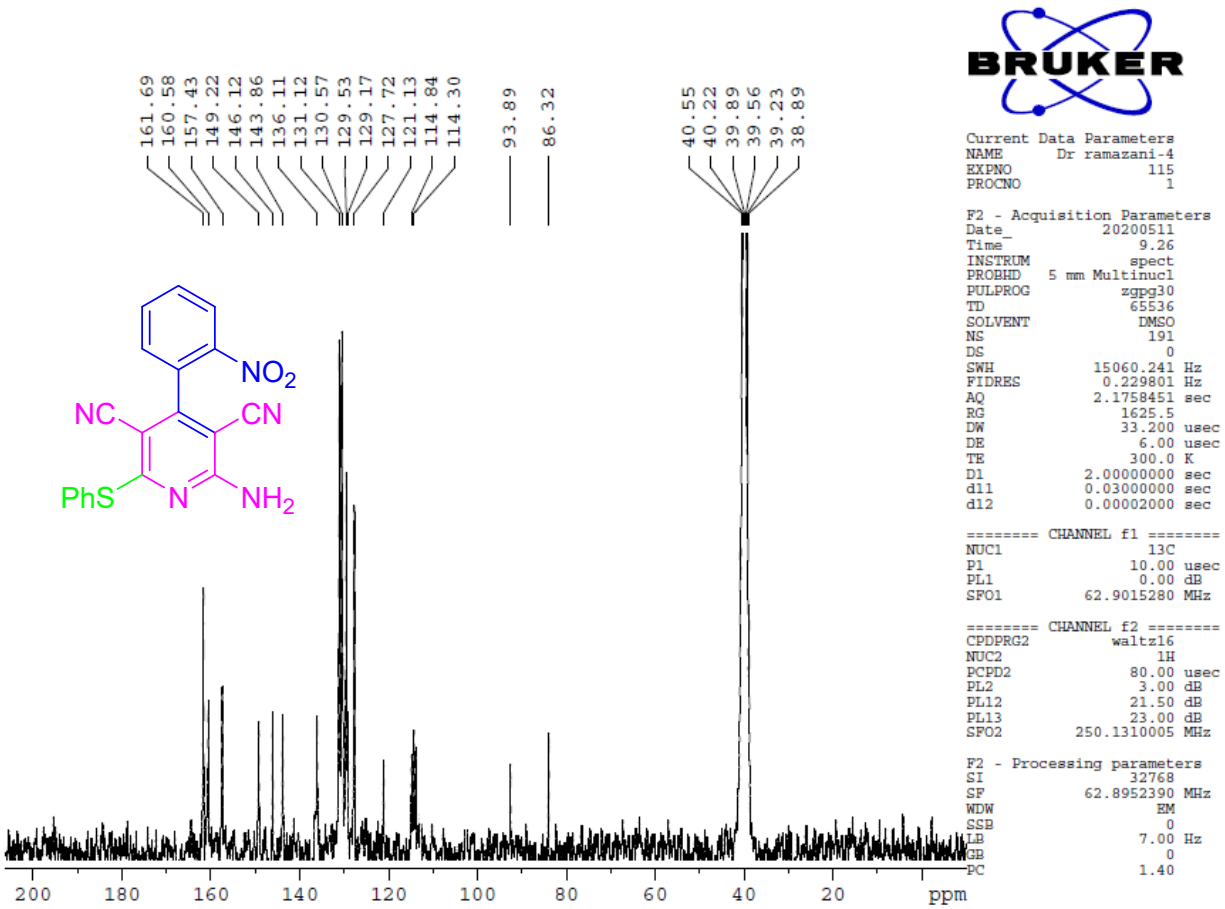


Figure S24. ^{13}C NMR spectrum of 2-amino-6-((2-nitrophenyl)thio)-4-henylpyridine-3,5-dicarbonitrile (**4l**)